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Cleavage of Acyclic Diaminocarbene Ligands at an Iridium(III) Center. Recognition of a New Reactivity Mode for Carbene Ligands

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Reaction of [Ir(*μ*-Cl)(ppy)2]2 (**1**) with 4 equivs of CNС6H4X (X = F **2a**, Cl **2b**,Br **2c**,I **2d**) in the presence of 2 equivs of AgOTf in dichloromethane at 20–25 °C furnished the *bis*isocyanide complexes [Ir(ppy)2(CNС6H4X)2](OTf) ([**3a**–**d**](OTf); 72–87%). Reaction of [**3a**–**d**](OTf) with an excess of gaseous ammonia at room temperature gave the *bis*diaminocarbene species [Ir(ppy)2{C(NH2)NHС6H4X}2](OTf) [**5a**–**d**](OTf) (73–83%); the two-step addition proceeds through an intermediate formation of appropriate monocarbene complexes [**4a**–**d**](OTf). Further reaction of [**5a**–**d**](OTf) with an excess of gaseous ammonia at 50 °C led to the cleavage of one diaminocarbene ligand to the cyanide ligand in [Ir(ppy)2(CN){C(NH2)NHС6H4X}] (**6a**–**d**) and this transformation is accompanied with the elimination of a substituted aniline. Treatment of [**5a**–**d**](OTf) with N(CH2CH2OH)3 at 50 °C resulted in the cleavage of the diaminocarbene ligand to the isocyanide and uncomplexed NH3; isocyanide remains bound to the iridium(III) center in [Ir(ppy)2{C(NH2)NHС6H4X}(CNС6H4X)](OTf) (**4a**–**d**). All isolated compounds were characterized by elemental analyses (C, H, N), molar conductivity measurements, TG/DTA, HRESI+/–-MS, FTIR, 1D (1H, 13C{1H}, 19F{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, 1H,13C-HMBC) NMR, and also by X-ray diffraction (for the *bis*isocyanide **3**, the *mono*diaminocarbene **4**, the *bis*diaminocarbene **5**, and the cyanide **6** type complexes).

Introduction

Acyclic diaminocarbenes (ADCs) are powerful ancillary ligands with a broad spectrum of applications in organometallic chemistry and catalysis.1-6 The catalytic efficiency of metal-ADCs is usually attributed to their strong electron-donating ability, steric control, and rotational flexibility of the ADC fragment.1, 3 Much less consideration has been given to the own reactivity of metal-ADC species, although an understanding of their reactivity would aid the elucidation of the reaction mechanism. This would in turn aid the rational design of new catalysts for a specific application.

While ADCs are usually considered as chemically and thermally stable, several reports indicate that they can exhibit at least three different reactivity patterns. The first reactivity mode is the backward conversion of the aminocarbene ligand to the starting isocyanide. Addition of an amine to an FeII-activated isocyanide leads to the monodentate ADC species that exist in dynamic equilibrium with the starting isocyanide complex (Scheme 1, Route A1).7, 8 A similar reversibility was observed for the related RuII species.9A dynamic equilibrium between the chelated *bis*(carbene)- and *mono*carbene-isocyanide PdII complexes (Route A2) was previously described.10 Steric repulsion between the backbone aryl groups of the carbene moieties has been suggested as a cause of the instability of the chelated ADCs, resulting in the ring opening.



**Scheme 1**. Reported reactivity types for the ADC ligands.

The second reactivity mode involves deprotonation of the protic ADC ligands. Herein, a reversible deprotonation of the protic metal-ADCs to give the corresponding ylide derivatives was described (Route B).11 Addition of acid restores the starting ADC ligand. Similar platinum12, 13 and palladium13, 14 carbene species are known to undergo deprotonation to give ylides.

In our group,15-18 the third reactivity mode of the ADC species was recently described: the double deprotonation of the NH moiety of the protic aminocarbene led to the generation of the bifunctional *N*-nucleophilic center that coupled concurrently with the carbon atom of CNR and the metal center in *cis*-[MCl2(CNR)2] complexes (M = PdII, PtII) to grant binuclear metal species (Route C). An unusual intramolecular regioisomerization of the structurally related (ADC)PdII complexes driven by the splitting of the C–N bond in the carbene fragment, was also reported.16



**Scheme 2**. Reported preparations of (ADC)IrIII complexes from (RNC)IrIII species.

Whereas palladium(II), platinum(II), and gold(I) ADC complexes are commonly obtained *via* the metal-mediated nucleophilic addition to isocyanides, corresponding route to iridium-bound aminocarbenes is limited to only but a few examples.2 Thus, “Chugaev-type” *bis*-cyclometalated iridium(III) complexes with *C,C*-chelated *bis*carbene ligands have been prepared via the addition of hydrazine to iridium(III) isocyanides (Scheme 2, Route D).19 In the second report,20 iridium(III) complexes with ancillary ADC ligands were obtained *via* the addition of primary- or unhindered secondary amines to (RNC)IrIII. Generation of an ADC ligand is accompanied by an *ortho*-metalation of its aryl moiety furnishing anionic *C*,*C*-chelated ADC-cyclometalated species (Scheme 3, Route E). Surprisingly, while the addition of ammonia, the simplest *N*-nucleophile, to metal-bound isocyanides is well-documented at palladium(II),21 platinum(II),21 and gold(I) centers,22 it has never been reported for iridium(III) center.

In the current report, upon generation of iridium-ADC complexes via the addition of ammonia to Ir-bound isocyanides, we observed a *selective* base-mediated cleavage of one or another C–N bond of the ADC ligand depending on conditions applied. This metal-mediated reaction represents a new reactivity mode for the acyclic diaminocarbene ligands and is discussed in the sections that follow.

Results and discussion

**Preparation of IrIII isocyanide species.**For our study, we obtained the new iridium(III) *bis*isocyanide complexes [Ir(ppy)2(CNС6H4X)2](OTf) (X = F [**3a**](OTf), Cl [**3b**](OTf), Br[**3c**](OTf), I[**3d**](OTf)) starting from the known23 [Ir(*μ*-Cl) (ppy)2]2 complex (**1**, ppy = (2-phenylpyridinato-C2,*N*)), and the corresponding isocyanides CNС6H4X (**2a**–**d**) (Scheme 3, Route F). The reaction of **1** with 4 equivs any one of **2a**–**d** in CH2Cl2 in the presence of 2 equivs of AgOTf at 20–25 °C afforded pure [**3a**–**d**](OTf) as pale yellow solids that were isolated in 72–87% yield. In this study, four different isocyanides were used to attest the scope of the processes described below.

Complexes [**3a**–**d**](OTf) are air- and moisture-stable at 20–200 °C; they are soluble in common aprotic solvents (e.g. CH2Cl2, CHCl3, and MeCN) and also in MeOH. Complexes [**3a**–**d**](OTf) were characterized by elemental analyses (C, H, N), molar conductivity measurements, TG/DTA, HRESI+-MS, FTIR, 1D (1H, 13C{1H}, 19F{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, 1H,13C-HMBC) NMR spectroscopy (see Supplementary Information for details).

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**Scheme 3**. Synthesis of *bis*isocyanide iridium(III) complexes [3a–d](OTf).

The solid-state structures of [**3b–с**](OTf) were elucidated by single-crystal X-ray diffraction (XRD) (Figure 1, left and center). Selected bond lengths and angles are shown in Table 1, and detailed crystallographic data are reported in the Supplementary Information (Table S1). In [**3b–с**](OTf), the iridium(III) center adopts a slightly distorted octahedral coordination environment, and the two nitrogen atoms of the ppy ligands are *trans* to each other. The (isocyanide)IrIII fragments are close to linear, and the angles ∠(Ir–C≡N) and ∠(C≡N–R) are 167.3(4)–176.6(3)° and 161.0(5)–176.8(3)°, respectively. A small distortion of these ligands from the linearity is presumably due to a negligible π back-donation from IrIII to CNR.24 Close values for the CN bonds distances in [**3b–с**](OTf) and in the respective free isocyanides **2b–с** (1.1552(11) in **2b** and 1.1544(17) in **2c**)25 as well as an increase in the CN stretching vibration frequency on going from the uncomplexed to the coordinated CNR species (Table S1, SI) support this observation. The Ir–Cisocyanide and CN bonds distances are 1.991(5)–2.019(3) and 1.146(4)–1.170(6), and are similar to those reported for other iridium(III) complexes bearing *tert-*butyl26 and aryl27, 28 isocyanides. The Ir−C bonds with the aryl isocyanides ligands in [**3b–с**](OTf) are slightly shorter than those involving the ppy ligands (2.050(3)−2.070(3) Å).

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**Figure 1.** View of [**3b**](OTf) (left), [**3c**](OTf) (center), and [**5b**](OTf)•СHCl3 (right) with the atomic numbering schemes. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels, the counter anions, and solvent molecules are omitted for simplicity.



**Scheme 4**. The reaction between [3a–d](OTf) and NH3

**Iridium(III)-mediated addition of ammonia to isocyanide**. In this study, the reaction of the representative complex [**3c**](OTf) with gaseous NH3 in СD2Cl2 was monitored by 1H NMR at room temperature (RT). After 2 h, generation of [**4c**](OTf) (55% 1H NMR yield) featuring one ADC ligand was confirmed (Scheme 4, Route G). After ca. 8 h, the presence of *bis*carbene complex [**5c**](OTf) (45% 1H NMR yield) in a mixture with [**4c**](OTf)(55% 1H NMR yield) were detected (Scheme 4, Route H). At RT, the addition of NH3 to the second isocyanide in [**4c**](OTf) proceeds at a comparable rate to that for the addition of the first equivalent of NH3 to the CNR in starting [**3c**](OTf). An inseparable mixture of [**4c**](OTf) and [**5c**](OTf) was formed, preventing the isolation of pure [**4c**](OTf). The complete transformation of [**4c**](OTf)to [**5c**](OTf) upon reaction with NH3 was achieved after 3 d. Solvent variation led to shortening the reaction time and to the improvement of the selectivity. Thus, the reaction of [**3a**–**d**](OTf) with NH3 in MeOH at RT for 12 h resulted in the nearly quantitative formation of [**5a**–**d**](OTf) as detected by 1H NMR. For comparison, we evaluated the reactivity of [Ir(ppy)2(CNR)2](OTf) featuring less electron-deficient RNCs [R = Cy, Xyl, Mes] and found that these complexes do not react with gaseous NH3 even upon prolonged heating (1,2-dichloroethane, 50 °C, 10 d).

ADC complexes [**5a**–**d**](OTf) were isolated as pale yellow solids in 73–86% yields; they are air- and moisture-stable at 20–160 °C. Complexes [**5a**–**d**](OTf) were characterized by elemental analyses (C, H, N), molar conductivity measurements, TG/DTA, HRESI+-MS, FTIR, 1D (1H, 13C{1H}, 19F{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, and 1H,13C-HMBC) NMR spectroscopy (see SI). To aid the structure elucidation of [**5a**–**d**](OTf), 1H,15N-HSQC and 1H,15N-HMBC spectra of the representative complex [**5d**](OTf), were recorded. Inspection of the 1H,15N-HSQC spectrum (Figure 2) indicates the presence of two distinct N-environments at *ca*. 125 and 140 ppm correlating to three corresponding H-environments. These observations suggest that both NH2 hydrogens in each of the carbene moieties are nonequivalent due to the restricted rotation of the ADC ligands in [**5**](OTf), giving rise to two different hydrogen environments distinguishable by 1H NMR.

The solid-state structure of [**5b**](OTf)•СHCl3was studied by XRD (Figure 1, right). In [**5b**](OTf)•СHCl3, the Ir–Ccarbene distances (2.001–2.098 Å) are similar to those of the previously reported iridium ADC species (2.039−2.079 Å)19 and are slightly shorter than in related NHC complexes (2.117−2.124 Å)29 thus indicating a somewhat stronger interaction between the ADC ligand and the metal center. These bonds are slightly longer than those between Ir and Cisocyanide in [**3b**–**c**](OTf) (1.991–2.019 Å) evidencing an insignificant contribution of a π back-donation from IrIII to ADC-ligands.5 In [**5b**](OTf)•СHCl3, the carbene moieties are almost planar, and the angles around the carbene carbon atoms are close to 120° (114.3−131.2°); the C−N bonds of the diaminocarbenes (1.311(11)−1.357(11) Å) are intermediate between single (e.g., 1.469(10) Å in amines30) and double (e.g., 1.279(8) Å in imines30) CN bond distances.

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**Figure 2**. 1H,15N-HSQC NMR spectrum of [**5d**](OTf) in CDCl3. Matching N and H environments in F1 and F2 dimensions are indicated in color.

**Cleavage of the acyclic diaminocarbene ligands**.As highlighted in the Introduction, metal-ADC complexes are generally considered as thermodynamically and kinetically stable.3, 4 However, in this study we observed that subsequent interaction between [**5**](OTf) and excess of NH3 in CH2Cl2 led to the cleavage of one ADC ligand to cyanide and corresponding substituted aniline as detected by 1H NMR and HRESI+-MS (Scheme 5, Route I). After the cleavage of the C–N bond, the cyanide formed remains bound to the metal center at [Ir(ppy)2(CN){C(NH2)NHС6H4X}] (**6**). This conversion proceeds slowly, and almost quantitative 1H NMR yield of **6** were achieved after 8 d at RT. The conductance of the reaction between [**5a**–**d**](OTf) and NH3 at higher temperature (50 °C) in 1,2-dichloroethane or MeOH, where both [**5a**–**d**](OTf) and NH3 are well soluble, afforded **6a**–**d** in nearly quantitative 1H NMR yields after 3 d. Isolated yields for **6a**–**d** were 77–84%. Monitoring of the reaction between [**5**](OTf) and excess of NH3 in MeOD showed gradual accumulation of **6a**–**d** over time, and no any other products were detected (Table S3). In addition, no follow-up transformation of **6a**–**d** was observed even if the reaction time was extended for up to 6 d.

Intrigued by these results, we studied the reaction of different bases with [**5**](OTf) (Table S3) using MeOH as a solvent. Use of MeOH for these reactions is, on the one hand, justified by the solubility of starting materials, while on the other hand, allows conducting the reaction at 50 °C, being useful for the direct comparison of all the data obtained. Thus, the reaction of one equiv of [**5b**–**d**](OTf) with 2 equivs of *weaker* organic bases such as *N*-methylmorpholine, triethanolamine, or pyridine in MeOH at 50 °C resulted in the selective cleavage of the diaminocarbene ligand to furnish the ligated isocyanide and free ammonia (Route J). Similar results were obtained with ammonia buffer solution; ratio between [**5**](OTf):NH4Cl:(base used to generate the buffer) was 1:10:1 (Table S3). The concentration of free ammonia and subsequently the basicity of this solution is significantly lower when compared to pure NH3. In this reaction, the generated isocyanide remains bound to the metal center at [Ir(ppy)2{C(NH2)NHС6H4X}(CNС6H4X)](OTf) (**4**). At 50 °C, a nearly quantitative conversion of [**5b**–**d**](OTf) to [**4b**–**d**](OTf) in the presence of triethanolamine (1:2 ratio between [**5b**–**d**](OTf) and N(CH2CH2OH)3) in MeOH was achieved after 2 d. 1H NMR yields of [**4b**–**d**](OTf) were 99%, and the isolated yields were 78–82%. For all these bases studied, no follow-up transformation of [**4b**–**d**](OTf) was observed even if the reaction time was extended for up to 4 d. For [**5a**](OTf), this reaction led to a mixture of [**4a**](OTf) and [**3a**](OTf)in *ca.* 9:1 ratio. To mention, heating of [**5a**–**d**](OTf) at 50 °C in MeOH without any base added does not lead to [**4b**–**d**](OTf) even after 4 d, and only starting materials were recovered. This suggests that Route J observed in this study proceeds in a different manner from the Route A reported in the literature.

It is worth noting that Route J can formally be reversed, by allowing the reaction of [**4b**–**d**](OTf) with NH3 formed. However, we found that under the reaction conditions, the concentration of NH3 is very low, the equilibrium is essentially shifted toward [**4b**–**d**](OTf), and the reaction rate of the latter with NH3 is insignificant. However, when excess of gaseous NH3 was used toward [**4b**–**d**](OTf) in either CH2Cl2, dichloroethane or MeOH, a nearly quantitative conversion of [**4b**–**d**](OTf) to **6a**–**d**, was expectedly achieved. We also noted, that in this case, the reaction rates were comparable to those for the reaction of [**5b**–**d**](OTf) with NH3 via the Route I.

Reaction of [**5b**–**d**](OTf) with *stronger* base (Et3N or KOH, 2 equivs) in MeOH produced an 1:1 mixture of [**4b**–**d**](OTf) and **6a**–**d**. Almost quantitative conversion of [**5b**–**d**](OTf) to abovementioned mixture of products was achieved within 2 d (for Et3N) or 1 d (for KOH). We believe that in this case, the cleavage of the carbene ligand proceeds in a non-selective manner by the concurrent splitting of either C–NH2 or C–NHR bonds in the ADC fragment giving a mixture of [**4b**–**d**](OTf) and **6b**–**d**, correspondingly. Composition of the reaction mixture remain unchanged even if the reaction time was extended for up to 4 d. We also attempted to convert isolated complexes [**4b**–**d**](OTf) to corresponding species **6b**–**d** by the action of various bases, *i.e.* *N*-methylmorpholine, triethanolamine, pyridine, Et3N, or KOH. No reaction was observed even after 4 d at RT or at 50 °C upon addition of either weaker or stronger base in either equivalent amounts or in a large excess. In all cases, a gradual decomposition of [**4b**–**d**](OTf) giving a mixture of yet unidentified products occurred; no presence of **6b**–**d** or corresponding substituted anilines were detected among the products by HRESI+/–-MS or 1H NMR (in MeOD or CD2Cl2).

**Table 1.** Selected bond lengths [Å] and angles [°] for [**3b**](OTf), [**3c**](OTf), [**4b**](OTf), [**5b**](OTf)•СHCl3, and **6c**•СHCl3.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | [**3b**](OTf) | [**3c**](OTf) | [**4b**](OTf) | [**5b**](OTf)•СHCl3 | **6c**•СHCl3 | |
| Bond lengths, Å | | | | | | |
| Ir1−C1 | 2.064(4) | 2.050(3) | 2.063(8) | 2.067(9) | 2.075(9) | |
| Ir1−C12 | 2.056(4) | 2.070(3) | 2.041(6) | 2.074(8) | 2.050(6) | |
| Ir1−C23 | 1.991(5) | 2.003(4) | 2.095(9) | 2.088(8) | 2.094(6) | |
| Ir1−C30 | 2.002(5) | 2.019(3) | 2.001(7) | 2.088(9) | 2.091(9) | |
| C23−N3 | 1.170(6) | 1.158(5) | 1.315(10) | 1.328(11) | 1.320(9) | |
| C23−N4 | − | − | 1.341(10) | 1.357(11) | 1.346(12) | |
| C30−N4 | 1.156(6) | 1.146(4) | − | − | − | |
| C30−N5 | − | − | 1.133(9) | 1.311(11) | 1.137(10) | |
| C30−N6 | − | − | − | 1.356(11) | − | |
| Angles, ° | | | | | |
| Ir1−C23−N3 | 167.3(4) | 174.6(3) | − |  | − | |
| Ir1−C30−N4 | 173.7(3) | 176.6(3) | − |  | − | |
| C23−N3−C24 | 161.0(5) | 173.4(4) | − |  | − | |
| C30−N3−C31 | 165.5(5) | 176.8(3) | − |  | − | |
| Ir1−C30−N5 | − | − | 171.5(9) |  | 176.3(5) | |
| N3−C23−N4 | − | − | 117.0(8) | 114.3(7) | 112.8(6) | |
| N5−C30−N6 | − | − |  | 116.1(8) | − | |



**Scheme 5**. Cleavage of both C–N bonds of the ADC ligands in [**5a**–**d**](OTf).

X-ray data for the *bis*carbene complex [**5b**](OTf)•СHCl3 indicates that both ADC moieties are turned out of the iridium plane C1–C12–C30–C23–Ir1 (**Figures 1** and **S2**). The dihedral angle between the plane N3–C23–N4 and the plane C1–C12–C30–C23–Ir1 is 144(3)°, plane N5–C30–N6 and plane C1–C8–C15–C26–Ir1 is 28.7(3)°). Inspection of the X-ray data for *mono*carbene complexes [**4**](OTf) and **6c**•СHCl3 indicates that the ADC moieties are located in the iridium plane. These data show that the intramolecular repulsion in the complex [**5a**–**d**](OTf), could additionally contribute toward the cleavage of the ADC ligands.

Diaminocarbene complexes [**4b**–**d**](OTf) and **6a**–**d** were obtained as yellow or pale yellow solids, respectively. These compounds are air- and moisture-stable at 20–170 °C ([**4b**–**d**](OTf)) or 20–190 °C (**6a**–**d**). Complexes [**4b**–**d**](OTf) and **6a**–**d** were characterized by elemental analyses (C, H, N), molar conductivities (for [**4b**–**d**](OTf)), TG/DTA, HRESI+-MS, IR, 1D (1H, 13C{1H}, 19F{1H}) and 2D (1H,1H-COSY, 1H,13C-HMQC/1H,13C-HSQC, and 1H,13C-HMBC) NMR spectroscopy (see SI). The solid-state structures of [**4b**](OTf) and **6c**•СHCl3 were established by XRD (**Figure 3,** center and right). In [**4b**](OTf), the Ir–Cisocyanide bond (2.001(9) Å) is similar to the bonds between Ir and Cisocyanide in the isocyanide complexes **3a**–**d** (1.991–2.019 Å), whereas in **6c**•СHCl3, the Ir–CN bond (2.091(9) Å) is slightly longer. The Ir–Ccyanide bond (2.091(9) Å) in **6c** is similar to the previously reported the Ir–Ccyanide bonds in the complexes [Ir(dfppy)2(CNR)(CN)] (R = Xyl, *t-*Bu) (2.064(3)–2.074(3) Å)31 and substantially longer than in the complexes [Ir(ppy)2(CN)(PR3)] (2.048(6)–2.054(3) Å).29

As the next step, we attempted to rationalize our findings. Although the cleavage of R–NC bond of isocyanides leading to cyanide species was previously reported, it is limited to aliphatic alkyl species.32-34 Our findings suggest that [**5**](OTf) may be subject to a cleavage *via* two competing routes, viz. by the splitting of either C–N(H)R (Scheme 5, Route I) or C–NH2 (Route J) bonds in the carbene fragment. The ratio between [**4**](OTf) and **6** depends on the reaction conditions, and no interconversion between [**4**](OTf) and **6** occurs.

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**Figure 3.** View of [**4b**](OTf) (left), and **6c**•СHCl3 (right) with the atomic numbering schemes; thermal ellipsoids are drawn with the 50% probability. Hydrogen labels for both species, the disordered part of the molecule for **6c**•СHCl3 with less occupancy, and the solvent molecule are omitted for simplicity.

It is also known that addition of a base to the metal-ADC species, containing one hydrogen on each of the *N*-atoms of the carbene, can result in their reversible stepwise deprotonation.4, 11, 14, 18, 35-37 If N(H)–Aryl and N(H)–Alkyl moieties are present in the carbene fragment, the N(H)–Aryl moiety is deprotonated first (*i.e.* by KOH in CH2Cl2) owing to more electron-accepting character of an aryl substituent; deprotonation of the N(H)–Alkyl moiety requires much stronger base (*i.e.* by LiHMDS in THF).11, 36, 37 In our case, we believe that the addition of a *stronger* base, *i.e.* Et3N or KOH to the aminocarbene species [**5**](OTf) results in the concurrent non-selective deprotonation of either NH2 or NH–Aryl moieties of the ADC leading to a mixture of [**4**](OTf) and **6** (see SI, **Scheme S1**). Application of a *weaker* base, *i.e*. *N*-methylmorpholine or triethanolamine results in the selective deprotonation of the NH–Aryl moiety, that is subsequently converted into [**4**](OTf). In this case, the different acidity of CNH2 and CN(H)R groups are responsible for the observed reactivity: acceptor properties of aryl substituent make C–N(H)R group more acidic and prone to a deprotonation by a milder base (e.g., p*K*a for *p*-halogenanilines in DMSO is ca. 29,38 p*K*a for NH3 in DMSO is 4139). Insofar as the basicity of NH3 in organic solvents is comparable to that of Et3N,38 one can expect that the application of ammonia as a base should subsequently lead to a mixture of [**4**](OTf) and **6**. However, in our case, ammonia plays a *dual role* of a base, driving both Routes I and J, and a *nucleophile*. The reaction of [**4**](OTf) formed with an excess of NH3 present leads to the recovery of starting [**5**](OTf) by a reverse of the Route J. At the same time, Route I is irreversible insofar as the coordinated CN ligand does not react with NH3. As a result, when NH3 is used, the reaction proceeds until the full conversion of [**4**](OTf) to **6** is achieved.

Final Remarks

In pursuit of our studies on the chemistry of ADC metal complexes, we uncovered a new reactivity mode for the acyclic diaminocarbene ligands, *viz*. a competitive cleavage of either C–NH2 or C–NHR bonds in the aminocarbene fragment.

The reaction of [Ir(ppy)2{C(NH2)NHС6H4X}2](OTf) with an excess of gaseous NH3 in CH2Cl2 led to the cleavage of one ADC ligand to cyanide accompanied with the elimination of the corresponding substituted aniline. With a *weaker* organic base (e.g. *N*-methylmorpholine or triethanolamine), cleavage of the ADC ligand proceeded via an alternative route furnishing isocyanide and NH3. With a *stronger* base (e.g. Et3N or KOH), cleavage of the ADC ligands proceeds unselectively *via* both routes. Thus, whereas one can expect that cleavage of the ADC ligands via these two routes should proceed unselectively, we were able to discriminate the conditions when only one of these routes is predominant.

Our studies revealed that in the presence of a base acyclic diaminocarbene ligands can be converted into different types of ancillary ligands. Insofar as metal-ADC species are frequently used as catalysts for processes running under basic conditions, *i.e.* cross-coupling reactions, their reactivity should be cautiously weighted.

Experimental Section

**Materials and instrumentation.** Solvents, IrCl3•*n*H2O (Aldrich), 2-phenylpyridine (Alfa Aesar), and 14*M* aqueous solution of ammonia (Aldrich) were obtained from commercial sources and used as received. Complex **1** was prepared by the known method,23 that includes heating of IrCl3•*n*H2O at 110 °C with 2.5 equiv of 2-phenylpyridine in a 3:1 (v/v) mixture of 2-ethoxyethanol and deionized water.Isocyanides **2a**–**d** were synthesized by the published method.40,41 The C, H, and N elemental analyses were carried out on a ThermoFisher CHN analyzer. For CHN and XRD measurements (see below), single crystals of each compound were prepared upon slow evaporation of chloroform or dichloromethane solution of a title substance in air at RT. Mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source and MeOH was used as the solvent. The instrument was operated at positive ion mode using *m/z* range of 50–3000. The most intensive peak in the isotopic pattern is reported. Infrared spectra (4000–400 cm–1) were recorded on Shimadzu IRAffinity-1 FTIR spectrophotometer in KBr pellets. TG/DTA measurements were performed with a NETZSCH TG 209 F1 Libra instrument. The initial weights of the samples were in the range 2. 8–5.5 mg. The experiments were run in an open alumina crucible in a stream of argon at a heating rate of 10 K min−1. The final temperature of the experiments was 700 °C. Analysis of thermal data was performed with Proteus analysis software. 1D (1H, 13C{1H}, 19F{1H}) NMR spectra and 2D (1H,1H-COSY, 1H,1H-NOESY, 1H,13C-HMQC/HSQC, 1H,13C-HMBC, 1H,15N-HSQC, and 1H,15N-HMBC) NMR correlation experiments were conducted on Bruker AVANCE III 400 spectrometer in CDCl3 at 25 °C (at 400, 376, and 100 MHz for 1H, 19F, and 13C NMR, respectively). Chemical shifts are given in *δ*-values referenced to the residual signals of non-deuterated solvent (CHCl3), namely *δ* 7.26 (1H) and 77.2 (13C) and CCl3F *δ* 0.00 (19F). The 1H and 13C NMR data assignment for [**3a**–**d**](OTf)and [**5a**–**d**](OTf) was performed with the aid of 2D (1H,1H-COSY, 1H,1H-NOESY, 1H,13C-HMQC/HSQC, 1H,13C-HMBC, 1H,15N-HMQC/HSQC, and 1H,15N-HMBC) NMR correlation experiments.

**X-ray Structure Determinations.** An XRD experiment was carried out on Agilent Technologies Xcalibur ([**3b**](OTf),[**4b**](OTf),[**5b**](OTf)•СHCl3) and SuperNova ([**3a**](OTf), **6c**•СHCl3) diffractometers with monochromated MoKα or CuKα radiation, respectively. The crystal was kept at 100(2) K during data collection. The structures had been solved by the Superflip42, 43 structure solution program using Charge Flipping and refined by means of the ShelXL44 program incorporated in the OLEX2 program package.45 The unit cells of **6c•**СHCl3and[**4b**](OTf)also contains disordered molecules of solvent (Total Potential Solvent Accessible Void Volume 349 and 601 Å3; 136 and 322 electrons per cell for **6c**•СHCl3and [**4b**](OTf),respectively), that have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.46 Empirical absorption correction was applied in CrysAlisPro (Agilent Technologies, 2012) program complex using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. The crystallographic details are summarized in **Table S3** (Supporting Information). CCDC numbers 1538181 and 1538183–1538186 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Synthetic work and characterization**

**Synthesis of [3a–d](OTf).** A mixture of **1** (0.06 mmol) and AgOTf (0.112 mmol) was suspended in CH2Cl2 (5 mL), whereupon a solution of isocyanide **2a**–**d** (0.24 mmol) in CH2Cl2 (2 mL) was added dropwise. The reaction mixture was stirred at RT for 1 d to give a yellow solution containing a colorless precipitate of AgCl that was separated by centrifugation. The solution was then evaporated under vacuum at 20–25 °C to dryness, the solid formed was washed with diethyl ether (three 5-mL portions) and dried in air at RT.

[**3a**](OTf). Yield 75 mg (76%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.21 (d, *J*H,H = 7.5 Hz, 2H, H2), 6.93 (t, *J*H,H = 7.3 Hz, 2H, H3), 7.01−7.08 (m, 6H, H4 and H15), 7.46−7.51 (m, 6H, H14 and H10), 7.68 (d, *J*H,H = 7.6 Hz, 2H, H5), 8.00−8.04 (m, 4H, H8 and H9), 9.32 (d, *J*H,H = 5.8 Hz, 2H, H11). 13C{1H} ЯМР (CDCl3, δ): 116.79 (d, 2JC,F = 23.5 Hz, C15), 120.32 (C8), 123.80 (C4), 124.63 (C11), 124.76 (C10), 129.64 (d, 3JC,F = 8.8 Hz, C14), 130.38 (C2), 130.77 (C3), 132.95 (C12), 138.80 (C9), 143.78 (C6), 152.87 (C5), 154.48 (C1), 162.95 (d, 1JC,F = 253.1 Hz, C16), 167.32 (C7). 19F{1H} ЯМР (CDCl3, δ): –106.82 (s, 2F), –78.06 (s, 3F). IR (KBr, selected bands, cm–1): 2156 (s), 2184 (s) ν(C≡N). HRESI+-MS, *m/z*: calcd. for C36H24N4F2Ir+ 743.1593, found 743.1585 [M – OTf]+. Anal. calcd for: C37H24N4F5SO3Ir**•**0.5CH2Cl2: C, 48.21; H, 2.70; N, 6.00, found: C, 48.52; H, 2.60; N, 5.97. Λm = 138 Ohm–1 cm–1 mol–1. TG/DTA: 205–415 °C (weight loss 21%), 415–465 °C (weight loss 53,5%).

[**3b**](OTf). Yield 79.2 mg (72%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.20 (d, *J*H,H = 7.5 Hz, 2H, H2), 6.93 (t, *J*H,H = 7.4 Hz, 2H, H3), 7.03 (t, *J*H,H =7.6 Hz, 2H, H4), 7.33 (d, *J*H,H = 8.7 Hz, 4H, H15), 7.42 (d, *J*H,H = 8.7 Hz, 4H, H14), 7.49 (td, *J*H,H = 5.9 Hz, 2H, H10), 7.68 (d, *J*H,H = 7.6 Hz, 2H, H5), 8.00−8.05 (m, 4H, H8 and H9), 9.31 (d, *J*H,H = 5.8 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 120.40 (C8), 123.86 (C4), 124.66 (C11), 124.83 (C10), 124.93 (C13), 128.64 (C15), 129.77 (C14), 130.34 (C2), 130.80 (C3), 134.06 (C12), 136.35 (C16), 138.92 (C9), 143.74 (C6), 152.64 (C5), 154.37 (C1), 167.25 (C7). IR (KBr, selected bands, cm–1): 2151 (s), 2179 (s) ν(C≡N). HRESI+-MS, *m/z*: calcd. for C36H24N4Cl2Ir+ 775.1002, found 775.0965 [M – OTf]+. Anal. calcd for: C37H24N4Cl2F3SO3Ir**•**0.5CH2Cl2: C, 46.57; H, 2.61; N, 5.79, found: C, 46.25; H, 2.56; N, 5.78. Λm = 144 Ohm–1 cm–1 mol–1. TG/DTA: 210–381 °C (weight loss 10%), 381–530 °C (weight loss 67%).

[**3с**](OTf). Yield 98.6 mg (87%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.20 (d, *J*H,H = 7.5 Hz, 2H, H2), 6.93 (t, *J*H,H = 7.0 Hz, 2H, H3), 7.04 (t, *J*H,H = 7.1 Hz, 2H, H4), 7.37 (d, *J*H,H = 8.5 Hz, 4H, H15), 7.46 (t, *J*H,H = 6.0 Hz, 2H, H10), 7.50 (d, *J*H,H = 8.5 Hz, 4H, H14), 7.68 (d, *J*H,H = 7.8 Hz, 2H, H5), 7.99−8.04 (m, 4H, H8 and H9), 9.33 (d, *J*H,H = 5.9 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 120.45 (C8), 123.88 (C4), 124.43 (C16), 124.67 (C11), 124.86 (C10), 125.38 (C13), 128.75 (C15), 130.31 (C2), 130.80 (C3), 132.73 (C14), 134.27 (C12), 138.98 (C9), 143.73 (C6), 152.54 (C5), 154.28 (C1), 167.22 (C7). IR (KBr, selected bands, cm–1): 2151 (s), 2179 (s) ν(C≡N). HRESI+-MS, *m/z*: calcd. for C36H24N4Br2Ir+ 864.9971, found 864.9942 [M – OTf]+. Anal. calcd for: C37H24N4Br2F3SO3Ir**•**0.5CH2Cl2: C, 42.65; H, 2.39; N, 5.30, found: C, 42.76; H, 2.31; N, 5.15. Λm = 148 Ohm–1 cm–1 mol–1. TG/DTA: 200–378 °C (weight loss 9%), 378–560 °C (weight loss 69%).

[**3d**](OTf). Yield 104.4 mg (85%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.20 (d, *J*H,H = 7.5 Hz, 2H, H2), 6.93 (t, *J*H,H = 7.3 Hz, 2H, H3), 7.03 (t, *J*H,H = 7.6 Hz, 2H, H4), 7.21 (d, *J*H,H = 8.3 Hz, 4H, H15), 7.47 (td, *J*H,H = 6.1 Hz, 2H, H10), 7.66−7.71 (m, 6H, H5 and H14), 7.99−8.04 (m, 4H, H8 and H9), 9.31 (d, *J*H,H = 5.8 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 96.53 (C16), 120.30 (C8), 123.85 (C4), 124.63 (C11), 124.77 (C10), 126.14 (C13), 128.86 (C15), 130.40 (C2), 130.81 (C3), 134.35 (C12), 138.68 (C14), 138.80 (C9), 143.77 (C6), 152.84 (C5), 154.60 (C1), 167.28 (C7). IR (KBr, selected bands, cm–1): 2145 (s), 2173 (s) ν(C≡N). HRESI+-MS, *m/z*: calcd. for C36H24N4I2Ir+ 958.9714, found 958.9717 [M – OTf]+. Anal. calcd for: C37H24N4I2F3SO3Ir•0.5CH2Cl2: C, 39.16; H, 2.19; N, 4.96, found: C, 39.28; H, 2.12; N, 4.71. Λm = 137 Ohm–1 cm–1 mol–1. TG/DTA: 235–372 °C (weight loss 5,5%), 372–555 °C (weight loss 71,5%).

**Synthesis of [5a–d](OTf).** Complexes [**3a**–**d**](OTf) (0.02 mmol) were suspended in MeOH (3 mL) in glass vials that were placed in a larger scintillation flask (20mL) containing 5mL of aqueous ammonia (14*M*) at the bottom. After 1 d at RT, the solvent was evaporated under vacuum at 20–25 °C to dryness, the solid formed was washed with diethyl ether (three 2 mL-portions) and dried in air at RT.

[**5a**](OTf). Yield 13.5 mg (73%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.35 (d, *J*H,H = 7.5 Hz, 2H, H2), 6.84 (s, 2H, N−H), 6.89−7.04 (m, 12H, H3, H4, H15 andH14), 7.16 (s, 2H, N−H), 7.35 (t, *J*H,H = 5.8 Hz, 2H, H10), 7.68 (d, *J*H,H = 7.0 Hz, 2H, H5), 7.74 (s, 2H, N−H), 7.88 (t, *J*H,H = 7.3 Hz, 2H, H9), 7.95 (d, *J*H,H = 8.2 Hz, 2H, H8), 9.10 (d, *J*H,H =5.7 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 116.98 (d, 2*J*C,F = 22.8 Hz, C15), 119.59 (C8), 122.50 (C4), 124.06 (C10), 124.65 (C5), 127.59 (d, 3*J*C,F = 8.1 Hz, C14), 130.25 (C2), 131.26 (C3), 131.62 (C13), 136.98 (C9), 144.13 (C6), 152.51 (C11), 161.63 (d, 1*J*C,F = 248.7 Hz, C16), 165.00 (C1), 168.50 (C7), 194.35 (C12). 19F{1H} NMR (CDCl3, δ ): –112.87 (s, 2F), –78.28 (s, 3F). IR (KBr, selected bands, cm–1): 3248 (m), 3342 (m), 3442 (m) (ν(N−H). HRESI+-MS, *m/z*: calcd. for C36H30N6F2Ir+ 777.2124, found 777.2149 [M – OTf]+. Anal. calcd for: C37H30N6IrF5SO3: C, 47.99; H, 3.27; N, 9.08, found: C, 48.17; H, 3.10; N, 8.95. Λm = 135 Ohm–1 cm–1 mol–1. TG/DTA: 159–308 °C (weight loss 7%), 308–525 °C (weight loss 54%).

[**5b**](OTf). Yield 15.3 mg (80%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.35 (d, *J*H,H = 7.0 Hz, 2H, H2), 6.87 (d, *J*H,H = 8.5 Hz, 4H, H15), 6.91−7.01 (m, 6H, H3, H4 and N−H ), 7.23 (s, 2H, N−H), 7.29 (d, *J*H,H = 8.6 Hz, 4H, H14), 7.34 (t, *J*H,H = 5.8 Hz, 2H, H10), 7.68 (d, *J*H,H = 6.7 Hz, 2H, H5), 7.76 (s, 2H, N−H), 7.87 (t, *J*H,H = 7.2 Hz, 2H, H9), 7.94 (d, *J*H,H = 7.8 Hz, 2H, H8), 9.08 (d, *J*H,H = 5.5 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 119.60 (C8), 122.56 (C4), 124.09 (C10), 124.68 (C5), 126.65 (C15), 128.56 (C13), 130.22 (C14), 131.30 (C3), 133.43 (C2), 134.21 (C16), 137.01 (C9), 144.16 (C6), 152.52 (C11), 164.86 (C1), 168.44 (C7), 194.26 (C12). IR (KBr, selected bands, cm–1): 3250 (m), 3339 (m), 3445 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C36H30N6Cl2Ir+ 809.1533, found 809.1545 [M – OTf]+. Anal. calcd for: C37H30N6Cl2IrF3SO3: C, 46.35; H, 3.15; N, 8.76, found: C, 46.48; H, 3.02, N, 8.61. Λm = 135 Ohm–1 cm–1 mol–1. TG/DTA: 164–314 °C (weight loss 9%), 314–530 °C (weight loss 55%).

[**5c**](OTf). Yield 17.4 mg (83%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.35 (d, *J*H,H = 6.9 Hz, 2H, H2), 6.8 (d, *J*H,H = 8.5 Hz, 4H, H15), 6.91−7.01 (m, 6H, H3,H4 and N−H), 7.26 (s, 2H, N−H), 7.33 (t, *J*H,H = 7.5 Hz, 2H, H10), 7.41 (d, *J*H,H = 8.5 Hz, 4H, H14), 7.67 (d, *J*H,H = 6.9 Hz, 2H, H5), 7.74 (s, 2 H, N−H), 7.87 (t, *J*H,H = 8.2 Hz, 2H, H9), 7.93 (d, *J*H,H = 7.3 Hz, 2H, H8), 9.08 (d, *J*H,H = 5.3 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 119.59 (C8), 121.22 (C13), 122.55 (C4), 124.08 (C10), 124.67 (C5), 126.84 (C15), 130.20 (C2), 131.30 (C3), 133.19 (C14), 134.76 (C16), 137.00 (C9), 144.17 (C6), 152.56 (C11), 164.90 (C1), 168.42 (C7), 194.16 (C12). IR (KBr, selected bands, cm–1): 3250 (m), 3339 (m), 3445 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C36H30N6Br2Ir+ 899.0502, found 899.0480 [M – OTf]+. Anal. calcd for: C37H30N6Br2IrF3SO3: C, 42.41; H, 2.89; N, 8.02, found: C, 42.27; H, 2.93, N, 7.94. Λm = 139 Ohm–1 cm–1 mol–1. TG/DTA: 161–328 °C (weight loss 11%), 328–541 °C (weight loss 58%).

[**5d**](OTf). Yield 18.9 mg (81%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.34 (d, *J*H,H = 7.0 Hz, 2H, H2), 6.67 (d, *J*H,H = 8.1 Hz, 4H, H15), 6.93−7.01 (m, 6H, H3, H4 and N−H), 7.26 (s, 2H, N−H), 7.33 (t, *J*H,H = 6.4 Hz, 2H, H10), 7.62 (d, *J*H,H = 7.9 Hz, 4H, H14), 7.67 (d, *J*H,H = 7.3 Hz, 2H, H5), 7.72 (s, 2H, N−H), 7.89 (t, *J*H,H = 7.9 Hz, 2H, H9), 7.93 (d, *J*H,H = 7.6 Hz, 2H, H8), 9.07 (d, *J*H,H = 5.8 Hz, 2H, H11). 13C{1H} NMR (CDCl3, *δ*): 92.38 (C16), 119.60 (C8), 122.57 (C4), 124.09 (C10), 124.68 (C5), 126.95 (C15), 130.20 (C2), 131.31 (C3), 135.45 (C13), 137.01 (C9), 139.19 (C14), 144.47 (C6), 152.57 (C11), 164.87 (C1), 168.41 (C7), 194.11 (C12). IR (KBr, selected bands, cm–1): 3253 (m), 3339 (m), 3440 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C36H30N6I2Ir+ 993.0246, found 993.0267 [M – OTf]+. Anal. calcd for: C37H30N6I2IrF3SO3: C, 38.92; H, 2.65; N, 7.36, found: C, 39.07; H, 2.51, N, 7.22. Λm = 129 Ohm–1 cm–1 mol–1. TG/DTA: 163–319 °C (weight loss 14%), 319–534 °C (weight loss 62%).

**Synthesis of 6a–d.** Complexes [**5a**–**d**](OTf) glass (0.02 mmol) were suspended in 1,2-dichloroethane (3 mL) in small glass vials. Each vial with suspension of [**5a**–**d**](OTf) were placed in a larger scintillation flask (20mL) containing 5mL of aqueous ammonia (14*M*) at the bottom. Larger flasks were sealed and incubated at 50 °C for 3 d using circulation thermostat. After 3 d, solvent was evaporated under vacuum at 20–25 °C to dryness, the solid formed was washed with diethyl ether (three 2-mL portions) and dried in air at RT.

**6a**. Yield 10.5 mg (79%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.31 (d, *J*H,H = 6.9 Hz, 1H, CAr−H), 6.38 (d, *J*H,H = 6.9 Hz, 1H, CAr−H), 6.80 (td, *J*H,H = 7.1 Hz, *J*H,H = 0.9 Hz, 1H, CAr−H), 6.83−6.87 (m, 2H), 6.92 (td, *J*H,H = 7.4 Hz, *J*H,H = 0.8 Hz, 1H, CAr−H), 6.96−7.03 (m, 2H), 7.05−7.10 (m, 3H), 7.20 (t, *J*H,H = 6.3 Hz, 1H, CAr−H), 7.62 (dd, *J*H,H = 7.5 Hz, *J*H,F = 2.1 Hz, CAr−H), 7.75−7.83 (m, 2H), 7.89 (d, *J*H,H = 8.1 Hz, 1H, CAr−H), 7.92 (d, *J*H,H = 8.1 Hz, 1H, CAr−H), 8.49 (d, *J*H,H = 5.6 Hz, 1H, CAr−H), 9.75 (d, *J*H,H = 5.6 Hz, 1H, CAr−H); the N–H resonances were not detected. 13C{1H} NMR (CDCl3, *δ*): 117.06 (d, 2*J*C,F = 22.0 Hz, C15), 119.00, 119.49, 121.15, 121.96, 122.12, 123.05, 123.96, 124.41, 127.70 (d, 3*J*C,F = 8.8 Hz, C14), 129.47, 130.50, 130.70, 131.70, 132.25, 136.05, 136.20, 139.38, 143.55, 144.62, 151.82, 153.94, 160.77, 161.59 (d, 1*J*C,F = 248.7 Hz, C16), 165.45, 167.80, 169.81, 193.23 (Ccarbene). 19F{1H} NMR (CDCl3, *δ*): –112.73. IR (KBr, selected bands, cm–1): 2091 (s) ν(C≡N), 3340 (m), 3454 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C29H23N4FIr+ 639.1531, found 639.1538 [M – CN]+;calcd. for C30H24N5FIr+ 666.1539, found 666.1545 [M + H]+; calcd. for C30H23N5FIrNa+ 688.1459,found 688.1466 [M + Na]+. Anal. calcd for: C30H23N5FIr: C, 51.66; H, 3.44; N, 8.31, found: C, 51.48; H, 3.29, N, 8.19. TG/DTA: 184–352 °C (weight loss 6%), 352–594 °C (weight loss 49%).

**6b**. Yield 11.1 mg (81%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.30 (d, *J*H,H = 6.9 Hz, 1H, CAr−H), 6.38 (d, *J*H,H = 7.3 Hz, 1H, CAr−H), 6.80 (t, *J*H,H = 6.3 Hz, 1H, CAr−H), 6.84–6.99 (m, 5H, CAr−H), 7.08 (t, *J*H,H = 7.1 Hz, 1H, CAr−H), 7.20 (t, *J*H,H = 7.1 Hz, 1H, CAr−H), 7.35 (d, *J*H,H = 8.5 Hz, 2H, CAr−H), 7.62 (d, *J*H,H = 4.0 Hz, 1H, CAr−H), 7.63 (d, *J*H,H = 4.0 Hz, 1H, CAr−H), 7.75–7.83 (m, 2H, CAr–H), 7.89 (d, *J*H,H = 7.9 Hz, 1H, CAr−H), 7.93 (d, *J*H,H = 7.9 Hz, 1H, CAr−H), 8.66 (d, *J*H,H = 5.6 Hz, 1H, CAr−H), 9.76 (d, *J*H,H = 5.2 Hz, 1H, CAr−H); the N–H resonances were not detected. 13C{1H} NMR (CDCl3, *δ*): 119.02, 119.50, 121.17, 122.01, 122.11, 123.07, 123.97, 124.43, 126.78, 129.43, 130.28, 130.53, 130.73, 131.68, 133.46, 134.88, 136.06, 136.22, 143.53, 144.64, 151.80, 153.96, 158.09, 160.67, 165.41, 167.82, 169.83, 193.32 (Ccarbene). IR (KBr, selected bands, cm–1): 2091 (s) ν(C≡N), 3336 (m), 3448 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C29H23N4ClIr+ 655.1235, found 655.1204 [M – CN]+;calcd. for C30H24N5ClIr+ 682.1344, found 682.1310 [M + H]+; calcd. for C30H23N5ClIrNa+ 704.1163,found 704.1127 [M + Na]+. Anal. calcd for: C30H23N5ClIr: C, 50.43; H, 3.36; N, 8.11, found: C, 50.61; H, 3.28, N, 8.25. TG/DTA: 190–355 °C (weight loss 7%), 355–594 °C (weight loss 51%).

**6c**. Yield 12.0 mg (83%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.30 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 6.38 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 6.80 (t, *J*H,H = 6.2 Hz, 1H, CAr−H), 6.84–6.95 (m, 5H, CAr–H), 7.08 (t, *J*H,H = 6.6 Hz, 1H, CAr−H), 7.19 (t, *J*H,H = 7.2 Hz, 1H, CAr−H), 7.50 (d, *J*H,H = 8.5 Hz, 2H, CAr−H), 7.61 (d, *J*H,H = 4.9 Hz, 1H, CAr−H), 7.63 (d, *J*H,H = 5.5 Hz, 1H, CAr−H), 7.75–7.83 (m, 2H, CAr–H), 7.88 (d, *J*H,H = 8.1 Hz, 1H, CAr−H), 7.92 (d, *J*H,H = 8.1 Hz, 1H, CAr−H), 8.66 (d, *J*H,H = 5.6 Hz, 1H, CAr−H), 9.75 (d, *J*H,H = 5.8 Hz, 1H, CAr−H); the N–H resonances were not detected. 13C{1H} NMR (CDCl3, *δ*): 119.03, 119.51, 121.19, 122.02, 122.13, 123.08, 123.97, 124.44, 127.00, 129.48, 130.54, 130.71, 131.67, 133.27, 135.38, 136.08, 136.24, 143.53, 144.63, 151.79, 153.94, 160.62, 165.35, 167.79, 169.79, 193.24 (Ccarbene). IR (KBr, selected bands, cm–1): 2090 (s) ν(C≡N), 3339 (m), 3450 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C29H23N4BrIr+ 699.0730, found 699.0665 [M – CN]+;calcd. for C30H24N5BrIr+ 726.0839, found 726.0813 [M + H]+; calcd. for C30H23N5BrIrNa+ 748.0658,found 748.0616 [M + Na]+. Anal. calcd for: C30H23N5BrIr: C, 47.38; H, 3.15; N, 7.62, found: C, 47.11; H, 3.01, N, 7.51. TG/DTA: 187–359 °C (weight loss 9%), 359–601 °C (weight loss 55%).

**6d**. Yield 12.1 mg (80%), pale yellow solid. 1H NMR (CDCl3, *δ*): 6.30 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 6.37 (d, *J*H,H = 7.5 Hz, 1H, CAr−H), 6.79 (t, *J*H,H = 7.2 Hz, 2H, CAr−H), 6.86 (t, *J*H,H = 7.2 Hz, 2H, CAr−H), 6.92 (t, *J*H,H = 7.6 Hz, 1H, CAr−H), 7.08 (t, *J*H,H = 6.3 Hz, 1H, CAr−H), 7.20 (t, *J*H,H = 7.0 Hz, 1H, CAr−H), 7.61–7.64 (m, 2H, CAr–H), 7.70 (d, *J*H,H = 8.2 Hz, 2H, CAr−H), 7.75–7.83 (m, 2H, CAr–H), 7.88 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 7.92 (d, *J*H,H = 8.2 Hz, 1H, CAr−H), 8.65 (d, *J*H,H = 6.1 Hz, 1H, CAr−H), 9.74 (d, *J*H,H = 5.4 Hz, 1H, CAr−H); the N–H resonances were not detected. Insufficient solubility of **6d** precluded 13C{1H} NMR acquisition. IR (KBr, selected bands, cm–1): 2092 (s) ν(C≡N), 3340 (m), 3450 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C29H23N4IIr+ 747.0591, found 747.0616 [M – CN]+;calcd. for C30H24N5IIr+ 774.0700, found 774.0739 [M + H]+; calcd. for C30H23N5IIrNa+ 796.0520,found 796.0551 [M + Na]+. Anal. calcd for: C30H23N5IIr: C, 44.54; H, 2.96; N, 7.16, found: C, 44.69; H, 2.87, N, 7.01. TG/DTA: 197–361 °C (weight loss 13%), 361–598 °C (weight loss 58%).

**Synthesis of** [**4a–d**]**(OTf).** A mixture of [**5b**–**d**](OTf)(0.02 mmol) and triethanolamine (6 mg, 0.04 mmol) was suspended in MeOH (3 mL) and then stirred at 50°C (2 d) to give a yellow solution. The solution was then evaporated under vacuum at 20–25 °C to dryness, the solid formed was washed with diethyl ether and MeOH mixture (5:1, three 2-mL portions) and dried in air at RT.

[**4a**](OTf). Obtained in a mixture with 10% [**3a**](OTf), the spectral data are obtained by subtracting the corresponding spectra for [**3a**](OTf). Yellow solid. 1H NMR (CDCl3, *δ*): 6.21 (d, *J*H,H = 6.6 Hz, 1H, CAr−H), 6.38 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 6.91−7.01 (m, 6H, CAr−H), 7.03−7.09 (m, 3H, CAr−H), 7.31−7.37 (m, 3H, CAr−H), 7.44 (m, 1H, CAr−H), 7.50 (m, 1H, CAr−H), 7.70 (d, *J*H,H = 7.1 Hz, 2H, CAr−H), 7.95−7.99 (m, 3H, CAr−H), 8.04 (d, *J*H,H = 7.61 Hz, 1H, CAr−H), 8.91 (d, *J*H,H = 5.8 Hz, 1H, CAr−H), 9.46 (d, *J*H,H = 5.6 Hz, 1H, CAr−H), the N–H resonances were not detected. 13C{1H} NMR (CDCl3, *δ*): 116.40 (d, 2*J*C,F = 23.1 Hz), 117.10 (d, 2*J*C,F = 23.4 Hz), 119.72, 120.20, 120.65, 122.80, 123.48, 123.69, 124.40, 124.83, 124.97, 127.55 (d, 3*J*C,F = 8.6 Hz), 129.13, 129.39 (d, 3*J*C,F = 8.8 Hz), 130.33, 131.42, 132.11, 137.72, 137.94, 143.76, 144.24, 152.71, 155.85, 161.71 (d, 1*J*C,F = 252.4 Hz), 162.48 (d, 1*J*C,F = 253.2Hz), 166.34, 169.22, 189.30 (Ccarbene). 19F{1H} NMR (CDCl3, *δ*): –112.32 (s, 1F), –108.34 (s, 1F), –78.23 (s, 3F). HRESI+-MS, *m/z*: calcd. for C36H27N5F2Ir+ 760.1858, found: 760.1871 [M – OTf]+.

[**4b**](OTf). Yield 15.8 mg (84%), yellow solid. 1H NMR (CDCl3, *δ*): 6.20 (d, *J*H,H = 6.9 Hz, 1H, CAr−H), 6.36 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 6.86–7.06 (m, 8H, CAr–H), 7.27 (d, *J*H,H = 7.9 Hz, 2H, CAr−H), 7.32 (d, *J*H,H = 8.7 Hz, 2H, CAr−H), 7.41–7.45 (m, 1H, CAr–H), 7.68 (d, *J*H,H = 4.1 Hz, 1H, CAr−H), 7.70 (d, *J*H,H = 4.3 Hz, 1H, CAr−H), 7.93 (d, *J*H,H = 4.1 Hz, 2H, CAr−H), 7.98 (d, *J*H,H = 7.3 Hz, 1H, CAr−H), 8.03 (d, *J*H,H = 7.3 Hz, 1H, CAr−H), 8.88 (d, *J*H,H = 5.6 Hz, 1H, CAr−H), 9.45 (d, *J*H,H = 5.8 Hz, 1H, CAr−H); the N–H resonances were not detected. 13C{1H} NMR (CDCl3, *δ*): 119.33, 119.72, 120.21, 121.87, 122.84, 123.47, 123.76, 124.40, 124.84, 125.02, 125.88 (Cipso), 126.59, 128.56, 129.08, 129.48, 130.30, 130.35, 131.45, 132.09, 133.66, 133.97, 135.47, 137.75, 137.95, 139.72 (Cisocyanide), 143.70, 144.25, 152.66, 154.78, 155.64, 162.21, 168.26, 169.20, 189.16 (Ccarbene). IR (KBr, selected bands, cm–1): 2139 (s) ν(C≡N), 3336 (m), 3450 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C36H27N5Cl2Ir+ 792.1267, found 792.1260 [M – OTf]+. Anal. calcd for: C37H27N5Cl2IrF3SO3: C, 47.19; H, 2.89; N, 7.44, found: C, 46.95; H, 2.99; N, 7.19. Λm = 140 Ohm–1 cm–1 mol–1. TG/DTA: 179–334 °C (weight loss 8%), 334–575 °C (weight loss 49%).

[**4c**](OTf). Yield 16.9 mg (82%), yellow solid. 1H NMR (CDCl3, *δ*): 6.19 (d, *J*H,H = 6.9 Hz, 1H, CAr−H), 6.35 (d, *J*H,H = 7.3 Hz, 1H, CAr−H), 6.81 (d, *J*H,H = 8.2 Hz, 2H, CAr−H), 6.90–7.05 (m, 5H, CAr–H), 7.21 (d, *J*H,H = 8.7 Hz, 2H, CAr−H), 7.31 (t, *J*H,H = 6.6 Hz, 1H, CAr−H), 7.42 (d, *J*H,H = 8.5 Hz, 2H, CAr−H), 7.47 (d, *J*H,H = 8.5 Hz, 2H, CAr−H), 7.67–7.70 (m, 2H, CAr–H), 7.93 (d, *J*H,H = 4.0 Hz, 2H, CAr−H), 7.97 (d, *J*H,H = 7.3 Hz, 1H, CAr−H), 8.03 (d, *J*H,H = 7.9 Hz, 1H, CAr−H), 8.87 (d, *J*H,H = 5.3 Hz, 1H, CAr−H), 9.45 (d, *J*H,H = 5.6 Hz, 1H, CAr−H); the N–H resonanses were not detected. 13C{1H} NMR (CDCl3, *δ*): 119.75, 120.23, 120.64, 121.50, 122.87, 123.51, 123.57, 123.79, 124.42, 124.87, 125.04, 125.94 (Cipso), 126.40, 126.84, 128.76, 128.92, 129.09, 130.37, 131.48, 132.10, 132.47, 132.77, 133.30, 134.52, 137.79, 138.00, 139.97 (Cisocyanide), 143.73, 144.26, 152.68, 154.78, 155.59, 162.23, 166.28, 169.19, 189.13 (Ccarbene). IR (KBr, selected bands, cm–1): 2144 (s) ν(C≡N), 3336 (m), 3453 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. C36H27N5Br2Ir+ 882.0236, found 882.0232 [M – OTf]+. Anal. calcd for: C37H27N5Br2IrF3SO3: C, 43.12; H, 2.64; N, 6.79, found: C, 42.89; H, 2.73; N, 6.56. Λm = 145 Ohm–1 cm–1 mol–1. TG/DTA: 179–334 °C (weight loss 8%), 334–575 °C (weight loss 49%).

[**4d**](OTf). Yield 18.1 mg (78%), yellow solid. 1H NMR (CDCl3, *δ*): 6.19 (d, *J*H,H = 7.0 Hz, 1H, CAr−H), 6.35 (d, *J*H,H = 7.3 Hz, 1H, CAr−H), 6.67 (d, *J*H,H = 8.2 Hz, 2H, CAr−H), 6.91 (t, *J*H,H = 7.0 Hz, 1H, CAr−H), 6.95–7.04 (m, 3H, CAr−H), 7.06 (d, *J*H,H = 8.5 Hz, 2H, CAr−H), 7.30 (t, *J*H,H = 6.0 Hz, 1H, CAr−H), 7.40–7.43 (m, 1H, CAr−H), 7.63 (d, *J*H,H = 8.5 Hz, 2H, CAr−H), 7.65–7.69 (m, 4H, CAr−H), 7.93 (d, *J*H,H = 4.1 Hz, 2H, CAr−H), 7.96 (d, *J*H,H = 7.2 Hz, 1H, CAr−H), 8.02 (d, *J*H,H = 8.1 Hz, 1H, CAr−H), 8.86 (d, *J*H,H = 5.5 Hz, 1H, CAr−H), 9.44 (d, *J*H,H = 5.6 Hz, 1H, CAr−H); the N–H resonanses were not detected. 13C{1H} NMR (CDCl3, *δ*): 92.59 (C−I), 95.14 (C−I), 119.73, 120.20, 120.61, 122.85, 123.49, 123.77, 124.39, 124.85, 125.01, 125.91, 126.87, 127.02, 128.76, 128.87, 129.06, 130.34, 131.45, 132.07, 135.21, 137.76, 137.97, 138.39, 138.69, 139.25, 140.14 (Cisocyanide), 143.70, 144.24, 152.66, 154.76, 155.55, 162.22, 166.24, 169.16, 189.00 (Ccarbene). IR (KBr, selected bands, cm–1): 2145 (s) ν(C≡N), 3335 (m), 3448 (m) ν(N−H). HRESI+-MS, *m/z*: calcd. for C36H27N5I2Ir+ 975.9980, found 975.9995 [M – OTF]+. Anal. calcd for: C37H27N5I2IrF3SO3: C, 39.51; H, 2.42; N, 6.23, found: C, 39.59; H, 2.58; N, 6.31. Λm = 135 Ohm–1 cm–1 mol–1. TG/DTA: 181–345 °C (weight loss 13%), 345–578 °C (weight loss 58%).

Conflicts of interest

There are no conflicts to declare.

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